Publicized Report of Opening of Patent

Patent Application Disclosure No.
No 2000-117880
(P2000-117880A)
Opening Date: April 25, 2000

Int.Cl.		Distinguishing No.	F1		Theme Code
B 32 B	9/00		B 32 B	9/00	A 4F100
D 06 M	10/02		D 06 M	10/02	C 4L031
	11/46			11/12	

Request of examination: pending
Numbers of claim: 11 OL

Application number: H 10-293963
Date of application: October 15, 1998

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(Name of the invention)

Functional structure and manufacturing method for the same

(Object of the invention)

This invention offers a functional structure which maintains physical and chemical features and has excellent soil, odor, bacteria, and mildew resistance similar to fiber films and a manufacturing method for the same.

(Solution)

The functional structure of this invention has the following characteristics: a plasma polymer film is formed on a substrate and an opti-catalyst semi-conductor is formed on the surface of the film. The manufacturing method for this functional

structure has the following characteristics: a plasma polymer film is formed on a substrate and an opti-catalyst semi-conductor is formed on the surface of the film.
(Sphere of patent request)

(Claim 1)

Claim 1 is concerning a functional structure with the following characteristics: a plasma polymer film is formed on a substrate and an opti-catalyst semi-conductor is formed on the surface of the film.

(Claim 2)

Claim 2 is concerning the functional structure in claim 1 where the polymer film is fluorine based, silicon based, hydrogen carbide based, or acrylic acid based.

(Claim 3)

Claim 3 is concerning the functional structure in claim 1 or claim 2 where the plasma polymer film is at least 10 angstroms thick or more.

(Claim 4)

Claim 4 is concerning the functional structure in claim 1 to claim 3 where the plasma film is formed by low-pressure plasma treatment.

(Claim 5)

Claim 5 is concerning the functional structure in claim 1 to claim 4 where the opti-catalyst semi-conductor is at least one kind selected from TiO_2, ZnO, SnO_2, SiO_2, $SrTiO_3$, CdS, CdO, CaP, InP, In_2O_3, Ca As, $BaTiO_3$, K_2Nb_3, Fe_2O_3, Ta_2O_5, WO_3, SaO_2, Bi_2O_3, NiO, Cu_2O, SiC, MoS_3, InPb, RuO_2, or CeO_2.

(Claim 6)

Claim 6 is concerning the functional structure in claim 1 to claim 5 where the opti-catalyst semi-conductor is TiO_2.

(Claim 7)

Claim 7 is concerning the functional structure in claim 1 to claim 6 where the substrate is at least one kind of fiber or film.

(Claim 8)

Claim 8 is concerning the functional structure in claim 1 to claim 7 where the substrate is an organic polymer.

(Claim 9)

Claim 9 is concerning the functional structure in claim 1 to claim 8 where the functional structure is used for clothing, bedding, draperies, carpet, tatami (Japanese straw mat), tablecloths, walls, construction, sheets, tents, sailing canvas, flags, artificial turf, cover for professional réfrigerators, vehicle interiors, furniture, bags, or in the kitchen.

(Claim 10)

Claim 10 is concerning a manufacturing method for the functional structure where a plasma polymer film is formed on a substrate and an opti-catalyst semi-conductor is formed on the surface of the film.

(Claim 11)

Claim 11 is concerning a manufacturing method for the functional structure in claim 10 where the opti-catalyst is dispersed in resin.

Detailed explanation of the invention

[0001]

(Technical field of use)

This invention is concerning a functional structure which maintains physical and chemical features and has excellent soil, odor, bacteria, and mildew resistance similar to fiber films and a manufacturing method for the same.

[0002]

(Prior art)

Fiber structures such as fiber cloth or film-like laminations have long been used for clothes and for industrial applications. Regardless of the application, improvement in soil, odor, bacteria, and mildew resistance has been demanded, and various methods for obtaining these things have been suggested. For example, to improve soil resistance, the use of fluorine or silicon based hydrophilic materials or materials based on glycol has been suggested. These compounds cause pollution, and when the material is washed, they come off. For odor resistance, the use of absorbent materials such as activated charcoal or porous silica has been suggested. However, when these materials become saturated, the effect is like there is no deodorant at all. Materials can be used to prevent

odor. For example, it is well known that basic compounds like zinc oxide neutralizes hydrogen sulfide or methyl mercaptan which are acidic. Acidic materials like aluminum sulfide neutralizes bases like ammonia. These methods suffer from saturation as well, and they won't work at all on neutral compounds. Another solution is to decompose odorous materials into neutral ones. For example, iron/phtarothianin oxidizes ammonia. Hydrogen sulfide decomposes to sulfur, mercaptan becomes disulfide, aldehyde becomes carbonic acid, and amine becomes ketone and ammonia. However, some of these products of decomposition are also malodorous. There is almost nothing that will work on tobacco smoke or perspiration. Products of combustion of tobacco have several thousand components and it is difficult to counteract all of these. None of these current deodorizing methods are satisfactory.

[0003]

For anti-bacterial performance, ceramics with silver or copper or various organic compounds are used as disinfectants. However, there are limits on the type of bacteria that are killed. There are also safety problems with the disinfectants themselves.

[0004]

As stated above, there are many problems attaining the required soil, odor, bacteria, and mildew resistance simultaneously.

[0005]

Recently, the use of oxidation-reduction reactions of optical semiconductors such as titanium oxide has been suggested. This has been shown to decompose various organic impurities and NO_x and SO_x gas. Products which sinter titanium oxide on inorganic substrates such as ceramics or glass are already on the market. If this method is used with an organic substrate, the substrate will be attacked by the same reactions that are used to attain soil, odor, bacteria, and mildew resistance. To solve these problems, the use of a substance that has the proper opti-catalyst properties such as aluminum or silicon between the titanium oxide and the substrate has been suggested. However, when this method is used with fibers, there are problems with bonding, and the texture is rough.

[0006]

(Problems that this invention tries to solve)

The inventors of this invention examined the prior art. It offers a functional structure which maintains physical and chemical features and has excellent soil, odor, bacteria, and mildew resistance similar to fiber films and a manufacturing method for the same.

[0007]

(Steps for Solution)

This invention uses the following steps to solve the above problems. A plasma polymer film is formed on a substrate and an opti-catalyst semi-conductor is formed on the surface of the film. The manufacturing method for this functional structure has the following characteristics: a plasma polymer film is formed on a substrate and an opti-catalyst semi-conductor is formed on the surface of the film.

[0008]

(State of practice of this invention)

The inventors of this invention made thorough research on this subject. As a result, they developed a functional structure with the physical and chemical properties of an organic substrate. This invention has excellent soil, odor, bacteria, and mildew resistance due to an opti-catalyst reaction. They found that if a cross-linked coating is formed between the substrate and the opti-catalyst semi-conductor film formed by plasma polymerization, the desired properties could be obtained.

[0009]

The "desired function" in this document means the desired performance with respect to soil, odor, bacteria, and mildew resistance. Preferably this invention attains these simultaneously.

[0010]

The substrate in this invention consists of an organic polymer or fiber and a film-like substrate. It can be fibrous, film-like, or a combination of the two.

[0011]

The fiber in this invention is a synthetic fiber such as polyester, polyamide, poly acrilonitril, polypropylene, polyethylene, polyvinyl chloride, fluorine, aramid, or sulfone fiber. It may also be a semi-synthetic fiber such as rayon or acetate or a natural fiber such as cotton, wool, silk, or linen. This invention includes knit fabric, non-woven fabric, thread, or rope made of individual or mixed fibers described above.

[0012]

Various common additives can be used for increased productivity and for optimizing manufacturing processes. For example, it is possible to use thermal stabilizers, anti-oxidants, photo-stabilizers, flame hardening agents, static preventers, plasticizers, viscosity control agents, colors, smoothing agents, anti-bacterial agents, mildew preventers, etc. This invention is especially effective on organic fibers which may be damaged by the opti-catalyst reaction.

[0013]

The film-like substance in this invention is a polyester, polyamide, polypropylene,

polyethylene, fluorine, silicon, polyimide, or polyvinyl chloride sheet. These sheets can be formed by conventional methods such as solvent-based knife coating, extrusion, or calendaring.

[0014] Various common additives can be used for increased productivity and for optimizing manufacturing processes. For example, it is possible to use thermal stabilizers, anti-oxidants, photo-stabilizers, flame hardening agents, static preventers, plasticizers, viscosity control agents, colors, smoothing agents, anti-bacterial agents, mildew preventers, etc. The method for including these additives is not limited specifically. They can be pasted individually, or each one can be formed directly on the fiber.

[0015]

This invention forms a film on the surface of, for example, fibers or a film-like substance by plasma polymerization, a chemical vapor deposition technique (called PVCD in the following). Polymerized substances are deposited by electrical discharge processes in a polymer gas atmosphere. In another method, the polymer is applied directly to the surface and polymerized and cross linked by plasma. In this invention, the polymerized substance is cross-linked in three dimensions. It is extremely resistant to physical abrasion, and it is durable in the presence of the oxidation-reduction and the opti-catalyst reaction.

[0016]

Next, PCVD is explained in detail. Plasma is created by a high voltage discharge in the presence of a gas. There are plasma processes which take place at atmospheric pressure and reduced-pressure vacuum processes. Both types of process can be used in this invention. Vacuum process are run at pressures of 20 Torr or less, preferably 0.1 to 5 Torr. The voltage can be AC or DC. Low frequency, high frequency, or microwave alternating current can be used. The process gas can be a hydrogen carbide such as methane, ethane, ethylene, or acetylene; an acryl based gas such as acrylic or methacrylic; a silicon based gas such as vinyl trimethoxy silane, methyl triethoxy silane, methyl trimethoxy silane; or a fluorine based gas such as CF_4, C_3F_6, C_3F_8, C_4F_8, C_2F_4, C_3F_6O. They can be used alone or they can be mixed. The polymerized substance deposited on the substrate will have the same components as these gasses.

[0017]

Other process gasses such as oxygen, nitrogen, argon, or helium may be used as long as they do not interfere with the effects of this invention.

[0018]

The polymer film in this invention is 10 or more angstroms thick, preferably 50 to 800

angstroms. If the film is less than 10 angstroms thick, the opti-catalyst reaction may affect the substrate.

[0019]

Plasma polymerization may be don on one or both sides of the substrate depending on the application.

[0020]

In this invention, an opti-catalyst semi conductor layer is formed on the plasma-polymerized film. The opti-catalyst film in this invention is affected by light, preferably UV, and an electron/hole pair is produced. The electron produced reduces surface oxygen and produces a super oxide ion. The hole oxidizes surface hydroxides and produces a hydroxide radical. This decomposes substances by an oxidation/reduction reaction, producing the desired soil, odor, bacteria, and mildew resistance.

[0021]

The opti-catalyst in this invention is at least one of the following: TiO_2, ZnO, SnO_2, SiO_2, $SrTiO_3$, CdS, CdO, CaP, InP, In_2O_3, Ca As, $BaTiO_3$, K_2Nb_3, Fe_2O_3, Ta_2O_5, WO_3, SaO_2, Bi_2O_3, NiO, Cu_2O, SiC, MoS_3, $InPb$, RuO_2, or CeO_2. Among these, TiO_2 is harmless, inexpensive, and chemically stable. There are two types of titanium oxide – anataze and rutil. The anataze type is better since it is more reactive.

[0022]

For reaction efficiency, the opti-catalyst particles should be 20nm or less and have 100 to 300 m^2/g surface area. The amount of catalyst should be at least 0.05 weight percent, preferably 1 weight percent or more.

[0023]

To improve the activity of the opti-catalyst or to improve the anti-bacterial property, it is possible to dope metal such as white gold, palladium, silver, copper, or zinc.

[0024]

The opti-catalyst semi-conductor in this invention can be applied by, for example, immersing the substrate in a water-based dispersion of titanium oxide. Excess solution is then removed, and after drying and thermal processing it can be attached to the surface of the structure. The opti-catalyst particles can also be dispersed in solvent-based or water-based resin and applied by conventional methods such as immersion, spraying, etc.

[0025]

The water-based and solvent-based resins that can be used include resins based on silicon, fluorine, melamine, epoxy, acryl, or acryl silicon. Silicon and fluorine based resins are good because they do not decompose easily when exposed to the opti-catalyst

reaction. It is possible to use amorphous titanium peroxide, zeolite, alkyl silicate, etc.
[0026]
Examples of practice
In the following, this invention is going to be explained in more detail using examples of practice and examples of comparison. These examples were evaluated by the following methods.
[0027]
(Decomposition of contamination)
Water-based red ink (manufactured by Pilot) was diluted in water to form a 20% concentration solution. Using this solution, a line was brushed on the surface and air dried. Next, it was exposed to sunlight, and the time required for the color to disappear was measured.
[0028]
(Contamination, yield strength retention)
The samples were exposed at 45 degrees in an exposing stand as regulated in JIS A 1410 for 180 days.
[0029]
(1) contamination
The L value of the surface was measured before and after contamination using a digital color difference tester (manufactured by Suga Shikenki), and the degree of contamination was calculated using the following formula:
[0030]
degree of contamination = (a-b)/a x 100 where a is the L value before contamination and b is the L value after contamination. A greater value means greater contamination.
[0031]
(2) Tensile strength retention
A 3 cm wide tensile sample was measured before and after exposure. The degree of tensile strength retention was calculated by the method in JIS L 1017.
[0032] deodorant
80 μl of a 0.3% solution of ammonia water was dropped into a 500 cc quartz glass container that transmits UV. Next, a 5 cm x 5 cm sample was placed in the container, and the amount of ammonia remaining in 100 cc in the container was measured after 30 minutes using a gas detector (manufactured by GasTech), and the removal ratio based on the initial amount was calculated. Two samples were tested, one which was irradiated by a 5 mW/cm^2 UV source 7 cm from the sample, and one which was not irradiated.

[0033]

(anti-bacterial)

A stock liquid suspension of staphylococcus aureus 12732 was poured on a test sample, and the bacteria count after cultivation in a sealed container for 18 hours at 37 C was measured. The increase(decrease) from the initial bacterial count was found. Two samples were tested, one which was irradiated by a 0.08 mW/cm^2 UV lamp, and one which was not irradiated.

Examples of practice 1 to 12, and examples of comparison 1 to 7

A flat woven fabric which used 1000 denier 96 filament polyethylene terephthalate fiber (manufactured by Toray) for both directions was processed and heat set by conventional methods (thread density: 28/inch and 18/inch). This fabric was processed by the following treatments. Results are shown in table 1.

[0034]

A. The first layer process (plasma polymerization)

Equipment type: internal electrode

Anode: glass coated copper tube

Cathode: stainless steel drum

Frequency: 110 kHz – 13.56 mHz.

Vacuum level: 0.4 – 0.8 Torr

Energy density: 15 – 30 w/cm^2 (Based on the surface area of the electrode)

Gas flow: 100 – 300 cc/min

<P-1> Polymerization conditions: C_4F_8, 50 cc/min, 0.8 Torr, 13.56 mHz, 15 W/cm^2

Film thickness was controlled by controlling processing time

[0035]

<P-2> Polymerization conditions: acrylic acid, 50 cc/min, 0.8 Torr, 13.56 mHz, 15 W/cm^2

Film thickness was controlled by controlling processing time

[0036]

<P-3> Polymerization conditions: methane, 30 cc/min, 0.4 Torr, 500 kHz, 30 W/cm^2

Film thickness was controlled by controlling processing time

[0037]

<P-4> Polymerization conditions: vinyl trimethoxy silane, 30 cc/min, 0.4 Torr, 110 kHz, 18 W/cm^2

Film thickness was controlled by controlling processing time

[0038] Both sides of the clothe were treated

[0039]

(resin process)

<r-1> Using solvent based acryl resin (Chris Coat P113, manufactured by Dainippon Ink), knife coating was done on both sides of the fabric, and the thickness of the solid part was 15 um.

<r-2> water based olefin resin (ChemiPearl S 300, manufactured by Mitsui Sekiyu Kagaku), same treatment as r-1

[0040]

<r-3> fluorine based water and oil repellent (Asahi Guard AG710 manufactured by Meisei Kagaku) was used. It was processed by drip drying and cured so that the thickness of the solid part was 700 Angstroms. To improve the opti-catalyst process(a later step), the surface was made hydrophilic by a low-temperature nitrogen plasma process. The degree of water repellency was changed from 100 to 50 points.

[0041]

B. The second layer process

<t-1> The second layer was immersed in a water based dispersion of titanium oxide (opti-catalyst manufactured by Ishihara Sangyo, particle size: 20 nm, solid part: 40 %). The excess liquid was removed and the material was dried at 140 C. The amount of titanium oxide was 1.2%.

[0042]

<t-2> The same treatment was done using a water based dispersion of titanium/silicon composite oxide (manufactured by Nippon Shokubai, particle size: 12 nm, relative surface area: 150 m^2/g). The amount of opti-catalyst was 1.7%.

[0043]

Table 1

	Layer 1		Layer 2	Strength retention (%)	Decomposition (hr)	% contamination	Deodorant effectiveness		Anti-bacterial	
	resin	thickness	Opti-catalyst				irradiation	No irradiation	irradiation	No irradiation
Example of pract 1	p-1	8	t-1	45	5	78	95	12	4.5	0.9
2		16		46	5	81	93	9	3.9	1.3
3		55		52	4	75	85	13	4.1	2.0
4		230		66	5	81	97	4	4.2	0.5
5		710		69	4	75	93	7	4.6	1.1
6		980		74	5	83	97	1	4.1	0.3
7		790		65	4	80	95	11	4.1	0.6
8	p-2	85	t-1	55	5	88	97	4	4.4	1.2
9		110	t-2	56	4	81	92	8	4.4	0.8
10	p-3	240	t-1	62	5	78	91	2	4.1	0.3
11		180	t-2	57	5	88	85	9	3.8	0.6
12	p-4	590	t-1	73	4	81	92	12	4.2	0.6
Example of comp 1		-		41	>12	39	2	1	0.2	0.1
2		-		19	5	71	89	5	4.7	1.4
3		-		12	4	74	95	12	4.1	0.3
4		-		19	5	77	92	8	4.2	1.1
5		-		21	4	73	97	10	4.1	1.0
6		-		10	6	72	89	2	4.4	0.4
7		760		42	>12	32	1	1	0.4	0.1

From table 1, it was found that the first layers formed by the plasma polymerization methods in this invention controlled deterioration due to the opti-catalyst process while

providing the necessary soil, odor, bacteria, and mildew resistance

[0044]

example of practice 13, examples of comparison 8 and 9

An open weave stretch fabric was made using polyethylene terephthalate fiber (manufactured by Toray) with 1500 denier and 96 filaments. A vinyl chloride resin sheet 0.24 mm thick was molded at 170 C by calendaring methods. The resin compositions are shown in the following. It was thermally processed on both sides of the base cloth. After the coating process, roof material for sports facilities was manufactured.

[0045]

100 weight parts vinyl chloride resin (degree of polymerization was 1100)
45 weight parts di-2-ethyl hexyl phthalate
18 weight parts tricredil phosphate
12 weight parts antimony trioxide
8 weight parts titanium oxide (pigment)
1 weight part Chinubin 320 (UV absorbent)
2 weight parts epoxidized soy oil
2 weight parts Ba/Zn based stabilizer

The surface of the sheet was plasma polymerized under the following conditions using the plasma device used in example of practice 1, and an acryl based polymerized material 650 Angstroms thick was formed.

[0046]

Polymerization conditions: acrylic acid, 75 cc/min, 0.5 Torr, 350 kHz, 23 W/cm^2

Next, the following opti-catalyst liquid was used to coat the plasma polymerized surface. The amount of solid resin attached was 3.2%.

[0047]

30 parts Lumifron LF 200C (manufactured by ASAHI Glass)
6 parts isocyanate based curing agent
20 parts opti-catalyst titanium oxide (manufactured by Ishihara Sangyo)
44 parts tolulene

The sheet was left outside for 150 days the same as in example of practice 1, and soil resistance and tensile strength were measured. (example of practice 13)

[0048]

As an examples of comparison, one material did not receive plasma polymerization or the opti-catalyst process(example of comparison 8); and another material received only the opti-catalyst process without plasma polymerization (example of comparison 9) were

manufactured and evaluated the same as the examples of practice.

[0049]

Soil resistance and tensile strength were 8.6/92 in example of practice 13, 36.2/81 in example of comparison 8, and 9.5/68 in example of comparison 9.

[0050]

Example of practice 13 had less tensile strength loss than examples of comparison 8 and 9, and it had better soil resistance, making it a superior roofing material.

[0051]

(effects of this invention)

This invention offers a fiber, film like, or composite structure with the required soil, odor, bacteria, and mildew resistance by using an opti-catalyst process without degrading the chemical and physical properties of the base substrate. Material made using the methods in this invention is suitable for clothing or industrial use.

[0052]

Since this invention does not use polluting dyes, chlorine, bromine; is waterproof; and functions as an electromagnetic shield; it is environmentally friendly.

[0053]

This invention offers a fiber structure which is useful for luggage, bags, curtains, walls, water proof cloth, etc.